

4 Physical Behavior of Colloidal Particles

4.1 Brownian Motion

4.1.1 Translational Brownian Motion

Small solid particles, about 10^{-4} cm in size, can be introduced into a drop of liquid and then observed under a microscope. The particle is not at rest in the drop but is seen to be constantly moving about in a highly irregular way. The motion is a perpetual motion which seems to violate the second law of thermodynamics. Although this phenomenon seems to be first reported by a Dutch physician Jan Ingenhousz (Klafter et al., 1996), it is named as Brownian motion, since it was first investigated and reported by the Scottish botanist Robert Brown in 1827 as a physical phenomenon. However, he did not understand the origin of this phenomenon. Meanwhile Louis Bachelier developed a theory of Brownian motion in 1900 as a model of stock market fluctuation, but his work did not referred to the physical nature. After all, it remained for Albert Einstein in 1905 and for Marian Smoluchowski in 1906 to shed light into the phenomenon as due to random fluctuations to be expected even in thermal equilibrium.

In order to avoid any confusion in the description, consider that small solid particles are now in a large volume of liquid, which contains many liquid molecules. In the frame fixed to the volume at an absolute temperature T , the molecules move with thermal velocity \mathbf{v} , which obeys Gaussian distribution function,

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m\mathbf{v}^2}{2k_B T} \right) \quad (4.1)$$

where m is the molecular mass and k_B is Boltzmann's constant. This distribution is stationary and symmetric about $\mathbf{v} = 0$, where it has a pronounced peak. Thus, the average vanishes all the time, but the variance is finite, given by

$$\langle \mathbf{v}^2 \rangle = \frac{3k_B T}{m} \quad (4.2)$$

Therefore, molecules must exhibit a fluctuating velocity due to mutual collisions. A small foreign solid particle in the liquid is accordingly subject to a fluctuating net force due to collisions with those liquid molecules, and changes its pathway in an unpredictable zig-zagged form. The detailed pathway cannot be observed with any particle in the liquid, but it may be approximated by observing the location of the particle at a uniform interval of time and by connecting the observed positions successively by straight lines. If the time interval is reduced, the observed pathway is closer to the reality and shows the temporal history of the particle's motion.

The pathway of a Brownian particle is usually modelled by random walk. For simplicity, consider a particle which moves along a straight line and does not meet with any other solid particles (very dilute). Suppose that it has a probability $p = 1/2$ of taking a step to the right and a probability $q = 1/2$ of taking a step to the left. The probability is assumed not to depend on the history of previous behavior (the steps are statistically independent). Let us assume that the steps take place at a constant time interval of τ and the length of each step is l . Then what is the displacement x of the particle after N steps (time $t = N\tau$)? We can solve this problem by using induction.

Since the mean value of x , $\langle x \rangle$, is 0 for any value of N , the displacement can be meaningfully treated in terms of the variance, $\langle x^2 \rangle$. If we define $D \equiv l^2/2\tau$, $\langle x^2 \rangle_{N=1} = l^2 = 2 \cdot D \cdot \tau$ and $\langle x^2 \rangle_{N=2} = 2l^2 = 2 \cdot D \cdot 2\tau = 2Dt$, where $2\tau = t$ for $N = 2$. For $t = N\tau$, we then expect that

$$\langle x^2 \rangle_{t=N\tau} = 2Dt = l^2 N$$

Now, during time t , the particle makes N steps in a random order of the left or right (+ or -) step. Possible choices of the order can be such that the N steps may be all to the left, to the right, or are randomly mixed with + and - steps. We denote by X_m^N the displacement x after N steps of the particle in the m -th choice of the random order. Since the total number of different choices is 2^N , the variance of the displacement is given by

$$\langle x^2 \rangle_{t=N\tau} = \frac{1}{2^N} \sum_{m=1}^{2^N} (X_m^N)^2$$

For $t = (N+1)\tau$, we just add another step of the particle to either left or right and we have by induction

$$\langle x^2 \rangle_{t=(N+1)\tau} = \frac{1}{2^{N+1}} \sum_{s=\pm} \sum_{m=1}^{2^N} (X_m^N + s \cdot l)^2 = l^2 (N+1)$$

since $2\sum_{s=\pm} s \sum_{m=1}^{2^N} X_m^N$, which appears on expanding the square in the above equation, vanishes. Therefore, $\langle x^2 \rangle_{t=(N+1)\tau} = 2D(N+1)\tau$, or by induction we can write in general

$$\langle x^2 \rangle = 2Dt \quad (4.3)$$

Thus, the average of the squared displacement is proportional to time elapsed during the displacement.

Now Eq. 4.3 holds exactly within the model. If the number of particles are very large and they are assumed to move independently, according to the central limit theorem of probability theory the distribution of the displacement x is Gaussian with the variance of Eq. 4.3, given by

$$F(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (4.4)$$

This expression should be interpreted as the probability of finding the particle between x and $x+dx$ at time t if it is initially at $x = 0$. It is easy to extend Eq. 4.4 to a three-dimensional case ($\mathbf{r} = (x, y, z)$), when the particle behaves isotropically. We have

$$F(\mathbf{r}, t) = \frac{1}{\sqrt{4\pi Dt}^3} \exp\left(-\frac{\mathbf{r}^2}{4Dt}\right) \quad (4.5)$$

This is now the probability referring to the volume element $dx dy dz$ at \mathbf{r} at time t . Then, we have

$$\langle \mathbf{r}^2 \rangle = 6Dt \quad (4.6)$$

We see that $\langle xy \rangle = \langle xz \rangle = \langle yx \rangle = \langle yz \rangle = 0$.

In the above model, the particle can change discontinuously in direction and speed. Although the position changes continuously in time, $F(x, t)$ of Eq. 4.4 is accordingly not differentiable with respect x . (One of such nondifferentiable functions used in physics is the well-known Dirac δ function.) Nevertheless, the present treatment leads to a correct answer to the physical phenomenon, but strictly speaking, Brownian motion must be treated in terms of a probability theory which is known as a Wiener process (Kac and Logan, 1979). Ignoring the nondifferentiability in Brownian motion, we find, by partially differentiating Eq. 4.4, the following diffusion equation.

$$\frac{\partial F(x, t)}{\partial t} = D \frac{\partial^2 F(x, t)}{\partial x^2} \quad (4.7)$$

where D is a constant. For three dimensions,

$$\frac{\partial F(\mathbf{r}, t)}{\partial t} = D \nabla^2 F(\mathbf{r}, t) \quad (4.8)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z} \quad (4.9)$$

Consider $F(x,t)$ as a probability density of the solid particles at x and t . Then, D can be identified as a diffusion coefficient of the particles in the liquid. D has been introduced by defining $D = l^2/2\tau$, where l and τ apparently behave like the mean free path and the mean free time of the particle, respectively. However, l and τ can be hardly theoretically calculated, since the particle moves in a viscous fluid under a randomly fluctuating net force.

A macroscopic treatment of Brownian motion can be made in terms of the Langevin equation. For simplicity, assuming that the fluid molecules have a very short relaxation time, let us consider that the Brownian particle moves in one dimension and write

$$m \frac{dv}{dt} + \gamma v = f(t) \quad (4.10)$$

where m is now the mass of the particle. Here, $f(t)$ is the macroscopic version of the fluctuating force at t . We assume that the following Gaussian relation:

$$\langle f(t) \rangle = 0, \quad \langle f(t_1)f(t_2) \rangle = C\delta(t_2 - t_1) \quad (4.11)$$

where δ is the Dirac δ function, with properties $\delta(t_2 - t_1) = 0$ if $t_2 \neq t_1$ and $\int \delta(t_2 - t_1) dt_1 = 1$ if the integration covers the neighborhood of t_2 . Here, the constant C is so determined that the solution of Eq. 4.10 leads to a stationary Brownian motion. The constant γ is a damping or friction coefficient due to the viscous fluid. The inverse of γ is the mobility. Namely, in a stationary state, if the particle is moving with speed v in a viscous fluid under an external force f , $v = (1/\gamma)f$. The proportional constant $1/\gamma$ is called the mobility. Obviously, if $f(t) = 0$ all the time, Eq. 4.10 predicts that the particle slows down exponentially to rest.

In order to see that the solution of Eq. 4.10 represents Brownian motion, we solve it to obtain

$$v(t) = v(0)e^{-\frac{t}{s}} + \frac{1}{m} \int_0^t f(t')e^{-\frac{t-t'}{s}} dt' \quad (4.12)$$

where $s = m/\gamma$, a viscous relaxation time. Since the initial velocity $v(0)$ is not correlated to the fluctuating force, we have

$$\langle v(0)f(t') \rangle = 0 \quad (4.13)$$

Therefore, Eq. 4.12 leads to

$$\frac{m}{2} \langle v^2(t) \rangle = \frac{m}{2} \langle v^2(0) \rangle e^{-\frac{2t}{s}} + \frac{1}{2} \int_0^t dt' \int_0^{t'} dt'' \langle f(t') f(t'') \rangle e^{-\frac{2t-t'-t''}{s}} \quad (4.14)$$

Using Eq. 4.11, this equation can be simplified. Assuming that the particle approaches to the thermal equilibrium with the surrounding liquid as $t \rightarrow \infty$, we find that $\frac{1}{2}m \langle v^2(t) \rangle = \frac{1}{2}k_B T$ for $t \gg s$. Therefore,

$$C = 2\gamma k_B T \quad (4.15)$$

Integrate Eq. 4.12 by parts to obtain

$$x(t) - x(0) = v(0)s \left(1 - e^{-\frac{t}{s}}\right) + \frac{1}{\gamma} \int_0^t \left(1 - e^{-\frac{t-t'}{s}}\right) f(t') dt' \quad (4.16)$$

Using Eqs. 4.11, 4.13, and 4.15, we then have

$$\langle (x(t) - x(0))^2 \rangle = \langle v^2(0) \rangle s^2 \left(1 - e^{-\frac{t}{s}}\right)^2 + \frac{2k_B T}{\gamma} \int_0^t \left(1 - e^{-\frac{t-t'}{s}}\right)^2 dt' \quad (4.17)$$

For $t \gg s$, the first term is smaller than the second one on the right-hand side and we have

$$\langle (x(t) - x(0))^2 \rangle = 2 \frac{k_B T}{\gamma} t \quad (4.18)$$

Therefore, if the diffusion coefficient satisfies

$$D = \frac{k_B T}{\gamma} \quad (4.19)$$

we have the Einstein-Smoluchowski equation, Eq. 4.3 or 4.6, which is characteristic of Brownian motion. Eq. 4.19 is known as Einstein's relation, which is one of many important equations attributed to Einstein. It provides a method of measuring the friction constant γ by experimentally determining the diffusion coefficient D .

For spherical solid particles of radius a , according to Stokes' law,

$$\gamma = 6\pi\eta a \quad (4.20)$$

where η is the viscosity of the liquid. This relation is obtained by assuming stick boundary conditions. We can then write the viscous relaxation time, s , for the particle as $2\rho a^2/9\eta$, where ρ is the density of the particle. The relaxation time is of the order of 10^{-9} s for a 0.1 μm sphere in water at room temperature. Therefore, if an experiment is capable of observing a shorter time than the time scale of $\rho a^2/\eta$, the fluid motion is unsteady and the diffusion coefficient must depend on time.

Under slip boundary conditions, $\gamma=4\pi\eta a$. Although stick boundary conditions are considered to hold for solid particles, slip boundary conditions seem to have a better agreement with gas bubbles with clean interfaces. The same seems to be true with organic solvent molecules or small particles in a solvent composed of molecules of the same size as those particles (Landau and Lifshitz, 1987; Bauer et al., 1974). In fact, according to Alder et al. (1970), molecular dynamics calculations on perfectly smooth elastic sphere give results (computer simulation), which agree with slip boundary conditions.

If the particles are spherical drops of fluid, the interfacial tension acting at the junction between the two immiscible fluids (say, oil droplets in water) tends to keep them spherical in shape for small droplets at the slow motion, but the molecules at the interfaces are dragged by the particle motion. Accordingly, the fluid inside the droplets will circulate internally and modifies the Stokes law. The internal motion, however, depends on the nature of the surface active agents, usually present as impurities at the interfaces and a surface viscosity, ε , may be defined. If the effect is included, Stokes' law must be replaced by (Dryden et al., 1956)

$$\gamma = 6\pi\eta a \frac{(\varepsilon/a) + 2\eta + 3\eta_i}{(\varepsilon/a) + 3\eta + 3\eta_i} \quad (4.21)$$

where η_i is the viscosity of the internal fluid. For an air bubble for which $\varepsilon = 0$ and $\eta_i \ll \eta$, $\gamma = 4\pi\eta a$. But, if the interface is contaminated, for instance, by a surfactant, ε can be large and the air bubble must behave like a solid sphere. Therefore, the value of ε depends on the interfacial conditions. A general mathematical formalism for hydrodynamically treating the fluid-fluid interfaces has been developed by Scriven (1960). However, the value of ε must be obtained by experimentally determining the terminal velocity of a fluid droplet suspended in liquid under gravity.

For non-spherical particles, the calculation of γ is difficult and often impossible. In addition, small particles in general rotate very fast while diffusing in fluid, so that their angle-averaged behavior is usually macroscopically important. Those particles diffuse like spheres of some radius. Such a radius may be called as a hydrodynamic radius, r_H , which may be treated like the radius, a , in Stoke's law, Eq. 4.20.

Theoretically speaking, the friction coefficient γ should be obtained by hydrodynamic calculations of drag forces on the particle moving in fluid. In general, the friction coefficient is a tensor, but the following general law is valid for slow motion of particles accompanied by dissipative process (Landau and Lifshitz, 1980). Namely, in this case, the drag can be written in the form of $6\pi\eta \sum_j a_{ij} v_j$ (\mathbf{v} is the velocity.), where a_{ij} is a symmetric tensor. (See, for instance, Eq. 4.53 for an ellipsoid. We may note that there is a purely mathematical proof of the symmetry (Happel and Brenner, 1973, p. 166)). The tensor, a_{ij} , can then be characterized by its principal values, a_1 , a_2 , and a_3 . Since small particles, in general, rotate very fast, the diffusion coefficient can be approximated by angle-averaged values, and we have

$$D = \frac{k_B T}{18\pi\eta} \left(\frac{1}{a_1} + \frac{1}{a_2} + \frac{1}{a_3} \right) \quad (4.22a)$$

Then, we define the hydrodynamic radius by

$$\frac{1}{r_H} = \frac{1}{3} \left(\frac{1}{a_1} + \frac{1}{a_2} + \frac{1}{a_3} \right) \quad (4.22b)$$

This is an interesting relation, suggesting that

$$\frac{1}{r_H} = \frac{2}{3} V^{-1} \int_V \frac{1}{r} dV \quad (4.23)$$

where the density of the particle is assumed to be uniform, and r is the distance from the geometrical center. The factor of 2 in Eq. 4.23 is introduced so that the result for a spherical particle is identical as given by Stoke's law. Mazer et al. (1980) have shown that Eq. 4.23 also gives exact results for prolate and oblate

Table 4.1 Diffusion coefficients of particles with various shapes (stick boundary conditions), angle-averaged over orientations. (Here a_G , radii of gyration, are also given.)

$$D = \frac{k_B T}{6\pi\eta a_H}, \quad (a_H: \text{hydrodynamic radius})$$

Sphere of radius a : $a_G = (3/5)^{1/2}a$, $r_H = a$

Ellipsoid of major semiaxis a and minor semiaxis b :^a

$$a: \text{axis of rotation (prolate): } a_G = \sqrt{\left(\frac{a^2+2b^2}{5}\right)}, \quad a_H = \frac{\sqrt{a^2-b^2}}{\ln[(a+\sqrt{a^2-b^2})/b]}$$

$$b: \text{axis of rotation (oblate): } a_G = \sqrt{\left(\frac{2a^2+b^2}{5}\right)}, \quad a_H = \frac{\sqrt{a^2-b^2}}{\tan^{-1}[\sqrt{a^2-b^2}/b]}$$

Circular disk of radius a and thickness l ($\rho=l/(2a)$):^b

$$a_G = \frac{(1+4\rho^2)^{1/2}}{2} a$$

$$a_H = (3a/2)[(1+\rho^2)^{1/2} + \rho^{-1} \ln[\rho + (1+\rho^2)^{1/2}] - \rho]^{-1}$$

Rigid rod of length l and radius a ($\rho=l/a$, $v = \ln(\rho)$) :

$$a_G = ((1+\rho^2)/6/2)^{1/2} a$$

$$a_H = l/[2v - 0.19 - 8.24/v + (12/v)^2]$$

^a F. Perrin (1936).

^b Mazer, et al. (1980).

ellipsoids obtained by Perrin (1936) (see Table 4.1). They have calculated approximate hydrodynamic radii for disks and rigid rods by using Eq. 4.23.

Examples of the angle-averaged diffusion coefficients of particles of various shapes are given in Table 4.1 (see Eq. 4.22b).

In experiments we must sometimes take into consideration that molecules of the dispersion medium may be absorbed or adsorbed to modify the shape and size of particles.

Viscosity strongly depends on temperature. For water, $\eta \sim 0.01$ poise at 20°C . If $a \sim 10^{-4} \text{ cm}$, the value of $s = m/\gamma$ is about 10^{-6} s or less. Therefore, a choice of $t \sim 1 \text{ s}$ satisfies the condition ($t \gg s$) for deriving Eqs. 4.18 and 4.19. We can experimentally check the validity of Eqs. 4.3 and 4.18 by observing Brownian displacements of the same particle under a microscope at an equal interval of time. In fact, J. Perrin (1909) found that Eq. 4.18 holds over wide ranges of T , a , and η . Such experiments provided the value of k_B , and from the known value of the universal gas constant, Perrin obtained a value of $6.44 \sim 8.0 \cdot 10^{23} \text{ mol}^{-1}$ for Avogadro's constant, very close to the presently accepted value of $6.022 \cdot 10^{23} \text{ mol}^{-1}$ (see Svedberg, 1928). For this observation, Perrin used monodisperse particles, which were patiently selected from 1 kg of gamboge by using centrifugation.

The diffusion equation Eq. 4.7 is very easily solved by using the Fourier transform.

$$F(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathcal{F}(k, t) e^{ikx} dk \quad (4.24)$$

Substituting this into Eq. 4.7, we obtain

$$\frac{\partial \mathcal{F}(k, t)}{\partial t} = -k^2 D \mathcal{F}(k, t) \quad (4.25)$$

By solving this and using Eq. 4.24, we find

$$F(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx - k^2 D t} dk, \quad (4.26)$$

$F(x, t)$ behaves like the Dirac δ function at $t = 0$, as follows.

$$F(x, 0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk = \delta(x) \quad (4.27)$$

Therefore, the distribution, Eq. 4.4, is a particular solution of Eq. 4.7, standing for the initial condition that the particle is at $x = 0$. Eq. 4.4 is equivalent to Eq. 4.26, which is useful in treating light scattering by a Brownian particle. The three-dimensional version of Eq. 4.26 is given by, for a constant D ,

$$F(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} e^{i\mathbf{k} \cdot \mathbf{r} - k^2 D t} d\mathbf{k} \quad (4.28)$$

where $d\mathbf{k} = dk_x dk_y dk_z$. We have assumed that $t \gg$ the viscous relaxation time and D is a constant. The Langevin equation uses the steady-state hydrodynamic friction force, assuming that the hydrodynamic response to the Brownian particle approaches quickly to the steady state. The distribution function, $F(\mathbf{r}, t)$, has a Fourier component in \mathbf{k} -domain, $\exp(-Dk^2 t)$, which decays with a time constant, $1/Dk^2$. If $k = |\mathbf{k}|$ is large, the decay constant can be smaller than the viscous relaxation time. The definition, $D = \langle (\Delta \mathbf{r})^2 \rangle / 6t$ (Eq. 4.6 and see Sec. 4.5) is introduced for $t \gg$ the viscous relaxation time (Eq. 4.18), but may be used to evaluate D from the solution of the Langevin equation for small t , and find that it will be different from that for long time. Therefore, we might consider that the effective diffusion coefficient is a function of \mathbf{k} (Fijnaut, 1981).

The quantities, D and \mathbf{k} , appear in the dynamic light scattering from the system of Brownian particles (Sec. 6.2.2, where \mathbf{k} is denoted by \mathbf{q}). The scattered light undergoes a frequency broadening of Dk^2 , where D is the diffusion constant of the Brownian particles and \mathbf{k} is interpreted as the scattering vector. Here, two different concepts, a Fourier component and a scattering vector, appear in terms of the same notation, \mathbf{k} . This is not accidental, but they are physically closely related to each other. Because of Eq. 4.6, the Brownian time constant, $1/Dk^2$, corresponds to the Brownian path length, such that $\langle |\Delta \mathbf{r}|^2 \rangle^{1/2} \approx 1/k$. This is an important relation in physically understanding the frequency broadening of Dk^2 . Namely, the position \mathbf{r} of a Brownian particle is changed abruptly in its direction at every strong collision with molecules of the medium, affecting the coherency of the scattered light, as discussed in Sec. 6.2.2. The scattering vector can be evaluated in experiments (Eq. 6.10). Hence, if the frequency broadening, Dk^2 , is measured, D can be determined.

We must note that Eq. 4.28 stands only for dilute solutions, so that there are no hydrodynamic and interparticle interactions among particles. Modification due to these interactions depends on whether or not there is a concentration gradient (so an osmotic force) or an external force acting on individual particles in the solution. If neither of them are present, it is called the self-diffusion, which may be defined by Eq. 4.6 or $D = (1/6)d\langle \mathbf{r} \cdot \mathbf{r} \rangle / dt$ (see Sec. 4.5), where \mathbf{r} is a three-dimensional vector. If the particle concentration increases, the neighboring particles appear more closely to an individual particle and at short times the Brownian motion is hindered mainly by the near-field hydrodynamic effects, provided the solvent molecules are small and the hydrodynamic disturbance propagates very fast. Accordingly, the short-time self-diffusion coefficient, D_s^0 , of hard spheres in a concentrated suspension is reduced with increasing concentrations, as given by (Batchelor, 1976)

$$D_s^0 = D_0(1 - 1.83\varphi) \quad (4.29a)$$

where φ stands for the particle volume fraction, defined by (particle volume) \cdot (the number density). This has an experimental support (Kitchen et al. 1976).

On the other hand, at sufficiently long times a steady-state distribution evolves and we have a long-time self-diffusion, D_s^∞ , given by Tokuyama and Oppenheim (1995) as, for hard spheres,

$$D_s^\infty = D_0(1 - 1.749\varphi)^2 \quad (4.29b)$$

Batchelor (1983) gave a similar expression.

At the intermediate times, the self-diffusion coefficient may become complicated, as suggested by Eq. 4.17. We can see that a Brownian particle moves through the surrounding particles, thereby generating an anisotropic distribution of neighbors and thermodynamic forces, such as an osmotic force, which hinder the diffusion.

When there is a gradient in the particle concentration or in the chemical potential, the gradient diffusion coefficient is defined by the flux density due to Brownian motion of the particles. Then, the coefficient increases, because of an osmotically driven expansion into a region of lower pressure, which is slightly larger than the hydrodynamic retardation. According to Batchelor (1976), for hard spheres,

$$D = D_0(1 + 1.45\varphi) \quad (4.29c)$$

experimental results with DNA in water of Anderson et al. (1978) and silica spheres in cyclohexane of de Kruif et al. (1987) support this theory within the experimental error. The DNA molecules seemed not to exhibit interparticle interactions. But, in general, both effects of osmotic and interparticle interactions depend strongly on the type of the interparticle potential. The long range repulsions increase the osmotic compressibility but decrease the hydrodynamic part. The net effect can be dramatic increase in the diffusion coefficient.

4.1.2 Rotational Brownian Motion

If a solid particle has a non-spherical shape or is internally anisotropic (if the boundary is sticky) and moving in a fluid, its orientation can be observed to irregularly fluctuate in space even in thermal equilibrium of the system. As a simple example, we will consider a particle of an ellipsoid of revolution with a uniform density (see Eq. 4.63 for details) and treat the Brownian rotation of the symmetry axis of revolution. Assuming that there is physically no preferred direction perpendicular to the symmetry axis, we will see that this rotation is important to introduce the rotational diffusion constant of the particle.

The orientation of an ellipsoid can be specified by a unit vector, \mathbf{u} , fixed to the particle along the symmetry axis. This vector can be expressed in turn in terms of spherical coordinates, θ and ϕ , in space. For the reorientation process in thermal motion, Debye (1929) developed a model, based on the assumption that the ellipsoid changes its orientation due to random collisions with fluid molecules.

Assuming that the rotational and the translational motion of the particle are independent, consider a hypothetical sphere of a unit radius which is space-fixed in orientation but with the center at the geometrical center of the ellipsoid. Since there are random collisions, the ellipsoid randomly rotates. The intersecting point of \mathbf{u} with the unit sphere moves around on the surface of the unit sphere. The motion of this point can be regarded as a random translational walk on the surface of the unit sphere, leading to the idea of applying the diffusion equation, Eq. 4.8, to the motion on the surface (see Favro, 1960, for the rigorous derivation, and Eq. 4.55). Using the spherical coordinates to express the rotation, we obtain the following rotational diffusion equation (for derivation see McQuarrie, 1976).

$$\frac{\partial F(\mathbf{u}, t)}{\partial t} = D_r \nabla_{\mathbf{u}}^2 F(\mathbf{u}, t) \quad (4.30)$$

where $\nabla_{\mathbf{u}}^2$ is the angular part of ∇^2 of Eq. 4.9.

$$\nabla_{\mathbf{u}}^2 = \frac{1}{\sin^2 \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right) \quad (4.31)$$

The coefficient, D_r , in Eq. 4.30 is the rotational diffusion coefficient for the ellipsoid (the rotation of the symmetry axis and a special case of Eq. 4.63).

The differential operator, $\nabla_{\mathbf{u}}^2$, is also known, in quantum mechanics, as $-\mathbf{L}^2$, \mathbf{L} being the orbital angular momentum operator with Planck's constant $\hbar = 1$, and the z component, L_z , of \mathbf{L} is given by $-i(\partial/\partial\phi)$. The mathematics involved must be familiar in quantum mechanics. The operator, \mathbf{L} , is sometimes called as the generator of infinitesimal rotations and \mathbf{L}^2 and L_z can also be expressed in matrix forms.

In Eq. 4.30, $F(\mathbf{u}, t)d\Omega$ is the probability of the ellipsoidal particle with orientation \mathbf{u} in the elementary solid angle $d\Omega (= \sin\theta d\theta d\phi)$ at time t . Equation 4.30 can be easily solved by separation of variables, assuming that we can write $F(\mathbf{u}, t) \equiv F(\mathbf{u})\exp(-D_r\lambda t)$, with a constant λ . Equation 4.30 then leads to

$$\lambda F(\mathbf{u}) = -\nabla_{\mathbf{u}}^2 F(\mathbf{u}) = \mathbf{L}^2 F(\mathbf{u}) \quad (4.32a)$$

The solution does not diverge only when λ satisfies the relation:

$$\lambda = l(l+1), \text{ with } l = 0, 1, 2, \dots$$

But the solution is not unique, unless it simultaneously satisfies

$$L_z F(\mathbf{u}) = -i(\partial/\partial\phi)F(\mathbf{u}) = mF(\mathbf{u}) \quad (4.32b)$$

where $m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$. Such a solution is called as the spherical harmonics, $Y_{lm}(\theta, \phi) = Y_{lm}(\mathbf{u})$, which are known as the solution of the following differential equation.

$$\nabla_u^2 Y_{lm}(\theta, \phi) = -l(l+1)Y_{lm}(\theta, \phi) \quad (4.33)$$

The spherical harmonics for positive and negative m are related, such that

$$Y_{l,-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi), \quad (m > 0) \quad (4.34)$$

Here, the superscript $*$ is the complex conjugate. Some spherical harmonics are listed in Table 4.2.

As general terminologies, the specific solution of an operator, like L^2 and L_z , is called the eigenfunction of the operator standing for the specified constant, called the eigenvalue, like $l(l+1)$ and m . Thus, Y_{lm} is the simultaneous eigenfunction of the operators, L^2 and L_z , standing for the eigenvalues, $l(l+1)$ and m , respectively.

The spherical harmonics have the following important properties.

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) = \delta_{l'l'} \delta_{m'm} \quad (\text{normalization}) \quad (4.35)$$

$$\delta(\mathbf{u} - \mathbf{u}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}(\mathbf{u}) Y_{lm}^*(\mathbf{u}_0) \quad (\text{completeness}) \quad (4.36)$$

where \mathbf{u}_0 can be the initial orientation and

$$\delta(\mathbf{u} - \mathbf{u}_0) = \delta(\theta - \theta_0) \delta(\phi - \phi_0) / \sin \theta \quad (4.37)$$

Since the spherical harmonics satisfies Eq. 4.36 and forms a complete set, any well-behaving function, including a general $F(\mathbf{u}, t)$, can be expanded in terms of $Y_{lm}(\theta, \phi)$. Thus, we can write

$$F(\mathbf{u}, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{lm}(t) Y_{lm}(\theta, \phi) \quad (4.38)$$

Table 4.2 Spherical harmonics for $l = 0, 1, 2$.

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}, Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin \theta = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}$
$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) = \sqrt{\frac{5}{16\pi}} \frac{2z^2 - x^2 - y^2}{r^2}$
$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \cos \theta \sin \theta = \mp \sqrt{\frac{15}{8\pi}} \frac{xz \pm iyz}{r^2}$
$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} \sin^2 \theta = \sqrt{\frac{15}{32\pi}} \frac{x^2 - y^2 \pm i(xy + yx)}{r^2}$

substituting this into Eq. 4.30 and using Eqs. 4.33 and 4.35, we find

$$A_{lm}(t) = \bar{A}_{lm} e^{-l(l+1)D_r t} \quad (4.39)$$

where \bar{A}_{lm} is a constant. Therefore, the general solution is given by

$$F(\mathbf{u}, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \bar{A}_{lm} Y_{lm}(\theta, \phi) e^{-l(l+1)D_r t} \quad (4.40)$$

If the initial orientation is assumed to be along \mathbf{u}_0 , by using Eq. 4.36 we find that $\bar{A}_{lm} = Y_{lm}^*(\mathbf{u}_0)$ and

$$F(\mathbf{u}, t | \mathbf{u}_0, 0) = \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}^*(\mathbf{u}_0) Y_{lm}(\mathbf{u}) e^{-l(l+1)D_r t} \quad (4.41)$$

This is the orientation distribution function for the particles due to the rotational diffusion, provided that they are initially at \mathbf{u}_0 .

If the initial orientation \mathbf{u}_0 is at $\theta_0 = 0$ and $\phi_0 = 0$, since

$$Y_{lm}^*(0, 0) = \sqrt{\frac{2l+1}{4\pi}} \delta_{m,0} \quad (4.42)$$

we have

$$F(\mathbf{u}, t | 0, 0) = \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} Y_{l,0}(\theta, \phi) e^{-l(l+1)D_r t} \quad (4.43)$$

This distribution function is used to make an angle-average of some physical quantity attached to a rotating cylindrical particle under Brownian motion when the rotation around the symmetry axis is ignored. The physical quantity includes the particle orientation (see below), the particle polarizability tensor in a special light-scattering case of a pure symmetric top particle (see Sec. 6.2.2), etc.

As an example, consider the Brownian behavior of the symmetry axis of the particle relative to the z axis. We take the average of $\cos \theta$, the cosine of the angle between them over the distribution of the orientation, Eq. 4.43. Since $\cos \theta = (4\pi/3)^{1/2} Y_{1,0}^*(\theta, \phi)$, by using Eq. 4.35 we find that

$$\langle \cos \theta \rangle = e^{-2D_r t} \quad (4.44)$$

For small θ and t ($\theta \ll 1$ and $D_r t \ll 1$), we have, by expanding Eq. 4.44 into power series,

$$\langle \theta^2 \rangle = 4D_r t \quad (4.45)$$

Note that this may be compared to the translational relation of Eq. 4.6, and $\langle \theta^2 \rangle$ is proportional to D_r .

With an analogy to the translational case, we can find that the rotational diffusion coefficient has the following relation.

$$D_r = k_B T / \gamma_r \quad (4.46)$$

where γ_r is the friction coefficient (inverse of mobility) for the rotation of the symmetry axis. This coefficient is equal in magnitude to the torque required to rotate the particle with unit angular velocity, in absence of Brownian motion.

F. Perrin (1934, 1936) calculated D_r of an ellipsoid of revolution with the major semiaxis a and the minor semiaxis b under stick boundary conditions:

$$D_r = \frac{3k_B T}{16\pi\eta a^3} \frac{(2 - \rho^2)G(\rho) - 1}{1 - \rho^4} \quad (4.47)$$

where, following Table 4.1, if the major axis a is along the symmetry axis,

$$G(\rho) = (1 - \rho^2)^{-1/2} \ln \frac{1 + (1 - \rho^2)^{1/2}}{\rho} \quad (\rho = \frac{b}{a} < 1; \text{prolate}) \quad (4.48)$$

If the minor axis b is along the symmetry axis,

$$G(\rho) = (\rho^2 - 1)^{-1/2} \tan^{-1}(\rho^2 - 1)^{1/2} \quad (\rho = \frac{a}{b} > 1; \text{oblate}) \quad (4.49)$$

For a sticky sphere of radius a ,

$$D_r = \frac{k_B T}{8\pi\eta a^3} \quad (4.50)$$

Hu and Zwanzig (1974) have performed hydrodynamic calculations of the rotational frictions of prolate and oblate ellipsoids using slip boundary conditions. For small ρ 's, the coefficients are much smaller than those under stick boundary conditions.

In general, the rotation can occur about any orientation different from the symmetry axis. Then, the diffusion coefficient depends on the particle orientation relative to the translational motion. Now, choose a particle-fixed system, X, Y, and Z, with the origin at the geometrical center of the particle. For simplicity, consider a slightly deformed sphere defined by

$$\frac{X^2 + Y^2}{a^2} + \frac{Z^2}{a^2(1 - \varepsilon)^2} = 1 \quad (4.51)$$

Here we note that for $\varepsilon > 0$ the spheroid is oblate and for $\varepsilon < 0$ it is prolate. Happel and Brenner (1973, p. 215) treated the translational and rotational motion under stick boundary conditions. When the particle is moving with velocity \mathbf{v} and angular velocity $\boldsymbol{\omega}$, the drag force and drag torque are given by, respectively,

$$\mathbf{F} = -\vec{\gamma} \cdot \mathbf{v}, \quad \boldsymbol{\tau} = \vec{\gamma}_r \cdot \boldsymbol{\omega} \quad (4.52)$$

where $\vec{\gamma}$ and $\vec{\gamma}_r$ are tensors expressed in dyadic forms by, respectively,

$$\vec{\gamma} = 6\pi\eta a \left[\vec{\mathbf{I}} \left(1 - \frac{2}{5}\varepsilon \right) + \frac{1}{5}\varepsilon \mathbf{k}\mathbf{k} \right] + O(\varepsilon^2) \quad (4.53)$$

$$\vec{\gamma}_r = 8\pi\eta a^3 \left[\vec{\mathbf{I}} \left(1 - \frac{6}{5}\varepsilon \right) + \frac{3}{5}\varepsilon \mathbf{k}\mathbf{k} \right] + O(\varepsilon^2) \quad (4.54)$$

Here, $\vec{\mathbf{I}}$ is the unit dyadic ($\mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j} + \mathbf{k}\mathbf{k}$) and \mathbf{i} , \mathbf{j} , and \mathbf{k} are unit vectors along the particle-fixed axes, X , Y , and Z , respectively, Z being the symmetry axis.

Note that Eqs. 4.53 and 4.54 are surprisingly accurate even for large values of ε , the error being less than 10% even for $\varepsilon \sim 1$ (Lamb, 1932). Since the tensors are closely related to the damping or friction coefficients, from these relations a general case of the translational and rotational diffusion coefficient may be approximately treated.

The most general calculation of the friction tensor, $\vec{\gamma}_r$, may be due to Edwardes (1892) for the ellipsoid expressed by $X^2/a^2 + Y^2/b^2 + Z^2/c^2 = 1$. A typical component of the diagonalized tensor is given by

$$\gamma_X = 16\pi\eta(b^2 + c^2)/3(b^2B + c^2C)$$

where

$$B = \int_0^\infty (b^2 + s)^{-3/2} (a^2 + s)^{-1/2} (c^2 + s)^{-1/2} ds$$

$$C = \int_0^\infty (c^2 + s)^{-3/2} (a^2 + s)^{-1/2} (b^2 + s)^{-1/2} ds$$

As we have noted associated with Eq. 4.22a, if particles are very small and rotate very fast like macromolecules (the rotational mode is also governed by the equipartition of energy in equilibrium), the translational diffusion coefficient must be used after averaging over the orientation.

With the aid of the above formulae and the expressions for the rotational diffusivity it is possible to estimate the particle size and shape from combined translational and rotational diffusivity measurements on dilute suspensions. The results may of course be very different from those of the dry particle. This method has

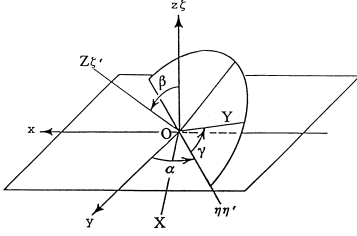


Fig. 4.1 Euler's angles between two sets of coordinates OXYZ (particle-fixed) and Oxyz (laboratory-fixed) (following the y-convention of Goldstein, 1980).

α : rotation about z axis to get $x \rightarrow \xi$, $y \rightarrow \eta$, $z \rightarrow \zeta$.

β : rotation about η axis to get $\xi \rightarrow \xi'$, $\eta = \eta'$, $\zeta \rightarrow \zeta'$.

γ : rotation about ζ' axis to get $\xi' \rightarrow X$, $\eta' \rightarrow Y$, $\zeta' \rightarrow Z$.

been applied to protein and virus particles (Shah, 1963; Dubbin et al., 1971; Bauer et al., 1975).

The rotational friction tensor, $\vec{\gamma}_r$, of a particle of a general shape is also symmetric and can be diagonalized, so that by dividing $k_B T$ by the principal values (Eq. 4.46 or Favro, 1960) we can construct corresponding principal components, D_{XX}^r , D_{YY}^r , and D_{ZZ}^r , of the rotational diffusion tensor in the particle-fixed coordinate system (OXYZ). However, in order to completely determine the orientation in space, the rotation of a set of the particle-fixed coordinates may be determined with respect to another laboratory-fixed set, x , y , and z , with the common coordinate origin. The relative specification can be made in terms of Euler's angles, α , β , and γ , defined in Fig. 4.1 following the y-convention. However, this choice of representation is inconvenient in the rotational diffusion, so that Favro (1960) used the Cayley-Klein parameters (Goldstein, 1980) in his derivation of the diffusion equation. As a result, it turns out that the Debye model for rotational diffusion can be applied for the general case and it can be written in terms of the Euler angles, referring to the particle-fixed principal axes, as

$$\frac{\partial F(\alpha, \beta, \gamma, t)}{\partial t} = -(D_{XX}^r J_X^2 + D_{YY}^r J_Y^2 + D_{ZZ}^r J_Z^2) F(\alpha, \beta, \gamma, t) \quad (4.55)$$

where $J_X^2 + J_Y^2 + J_Z^2 = \mathbf{J}^2$ is the square of the total angular momentum operator, \mathbf{J} . Here, variables are different from those of \mathbf{L} , as shown by Eqs. 4.31 and 4.32b and the differential forms are given by (Brink and Satchler, 1962).

$$\mathbf{J}^2 = -\frac{\partial^2}{\partial \beta^2} - \cot \beta \frac{\partial}{\partial \beta} - \frac{1}{\sin^2 \beta} \left(\frac{\partial^2}{\partial \alpha^2} + \frac{\partial^2}{\partial \gamma^2} \right) + \frac{2 \cos \beta}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha \partial \beta}$$

and

$$J_z = -i \frac{\partial}{\partial \alpha}, \quad J_z = -i \frac{\partial}{\partial \gamma}$$

As we have seen the case of \mathbf{L} in Eq. 4.30, we need only two variables, θ and ϕ , for the ellipsoid to uniquely specify the orientation and used two operators \mathbf{L}^2 and L_z . But now we have three variables, α , β , and γ . We need thus three (commuting) compatible operators to obtain unique solutions. (If we use the differential forms, we introduce separation of variables in Eq. 4.55 to obtain three ordinary differential equations, excluding the time part.) In the operator form, we note that the sets of Oxyz and OXYZ are equivalent in describing the magnitude of \mathbf{J} ($\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2 = J_X^2 + J_Y^2 + J_Z^2$). The magnitude of \mathbf{J} does not change since the system is isolated and in thermal equilibrium. Namely, \mathbf{J}^2 is constant under rotation. The orientation of \mathbf{J} in space can be specified by J_z (the z component) in the Oxyz system and by J_Z (the Z component) in the OXYZ system simultaneously with \mathbf{J}^2 . These three compatible operators offer the following three simultaneous operator equations. The normalized solutions, $D_{m,M}^{(j)}$, characterize the rotation by the eigenvalues, j , m , and M , as follows:

$$\mathbf{J}^2 D_{m,M}^{(j)} = j(j+1) D_{m,M}^{(j)}, \quad j = 0, 1, 2, 3, \dots \quad (4.56)$$

$$J_z D_{m,M}^{(j)} = m D_{m,M}^{(j)}, \quad m = -j, -j+1, \dots, -1, 0, 1, \dots, j-1, j \quad (4.57)$$

$$J_Z D_{m,M}^{(j)} = M D_{m,M}^{(j)}, \quad M = -j, -j+1, \dots, -1, 0, 1, \dots, j-1, j \quad (4.58)$$

The solutions form a complete orthogonal set. Writing $\boldsymbol{\Omega} = (\alpha, \beta, \gamma)$, we have

$$\delta(\boldsymbol{\Omega} - \boldsymbol{\Omega}_o) = \sum_{jmM} D_{m,M}^{(j)}(\boldsymbol{\Omega}_o) D_{m,M}^{(j)*}(\boldsymbol{\Omega}) \quad (4.59)$$

$$\int d\boldsymbol{\Omega} D_{m',M'}^{(j')*}(\boldsymbol{\Omega}) D_{m,M}^{(j)}(\boldsymbol{\Omega}) = \delta_{jj'} \delta_{mm'} \delta_{MM'} \quad (4.60)$$

Here,

$$\delta(\boldsymbol{\Omega} - \boldsymbol{\Omega}_o) = \delta(\alpha - \alpha_o) \delta(\beta - \beta_o) \delta(\gamma - \gamma_o) / \sin \beta \quad (4.61)$$

$$\int d\boldsymbol{\Omega} = \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma = 8\pi^2 \quad (4.62)$$

If $D_{XX}^r = D_{YY}^r = D_{ZZ}^r \equiv D_r$ (a spherical case), the particle rotation may not be important. But, if some noticeable axis is embedded in the sphere, the rotation may be treated by Eq. 4.30. If the principal values of the diffusion tensor are all different (an anisotropic case), the analytic solution cannot be obtained. However, if $D_{XX}^r = D_{YY}^r \equiv D_\perp^r$ and $D_{ZZ}^r \equiv D_\parallel^r$ (a symmetric top case), Eq. 4.55 reduces to

$$\frac{\partial F(\mathbf{\Omega}, t)}{\partial t} = -[D_{\perp}^r \mathbf{J}^2 + (D_{\parallel}^r - D_{\perp}^r) J_z^2] F(\mathbf{\Omega}, t) \quad (4.63)$$

If $F(\mathbf{\Omega}, t) \equiv F(\mathbf{\Omega})T(t)$ and $F(\mathbf{\Omega})$ is a simultaneous solution of Eqs. 4.56, 4.57, and 4.58, we can write the particular solution of Eq. 4.63 as

$$D_{m,M}^{(j)}(\mathbf{\Omega}) \exp(-[j(j+1)D_{\perp} + M^2(D_{\parallel} - D_{\perp})]t)$$

Thus, by taking the linear combination of this, we can obtain the general solution of Eq. 4.63. If the particle is initially oriented uniformly at $\mathbf{\Omega}_o = (0,0,0)$, the normalized distribution function of the orientations of the particles undergoing rotational Brownian motion is given by

$$F(\mathbf{\Omega}, t | \mathbf{\Omega}_o, 0) = \frac{1}{8\pi^2} \sum_{jmM} D_{m,M}^{(j)*}(\mathbf{\Omega}_o) D_{m,M}^{(j)}(\mathbf{\Omega}) e^{-(j(j+1)D_{\perp} + M^2(D_{\parallel} - D_{\perp}))t} \quad (4.64)$$

where $\mathbf{\Omega}_o = (0,0,0)$.

We note that, if $\gamma = 0$, β and α behave geometrically like θ and ϕ of polar angles (see Fig. 4.1). Thus, since $D_{m0}^{(j)}$ and Y_{lm} are normalized, from Eq. 4.62 we have ($j = l$)

$$D_{m,0}^{(j)}(\alpha, \beta, \gamma) = \sqrt{2\pi} Y_{jm}^*(\beta, \alpha)$$

4.1.3 Brownian Motion in Concentrated Suspensions

When we theoretically treat the coagulation or flocculation of particles, we must consider that particles approach each other while they are undergoing Brownian motion. Then, irrespective of the particle concentration, the hydrodynamic interactions among approaching particles must be important.

When solid particle density is large, hydrodynamic interactions among particles can be significant, affecting the Brownian motion and, consequently, diffusion. Happel and Brenner (1973) treated hydrodynamic interactions between two or more spherical particles. Ermak and McCammon (1978) and Hess and Klein (1978) treated their Brownian motion. The hydrodynamic interactions are long range in incompressible fluids, so that, if the suspension is dense, we must treat all of the particles simultaneously. Then, the Langevin equation for N Brownian particles (mass: m) numbered by i ($i = 1, 2, \dots, N$) reads as

$$m \frac{d\mathbf{v}_i}{dt} = - \sum_{j=1}^N \vec{\gamma}_{ij} \cdot \mathbf{v}_j + \mathbf{F}_i(t) + \sum_{j=1}^N \vec{\mathbf{g}}_{ij} \cdot \mathbf{f}_j \quad (4.65)$$

where \cdot implies the dot product and $\vec{\gamma}_{ij}$ is one of N^2 3×3 generalized friction tensors. The force, $\mathbf{F}_i(t)$, is the sum of interparticle (not hydrodynamic) and external forces acting on the i -th particle, while $\sum_j \vec{g}_{ij} \cdot \mathbf{f}_j$ represents the randomly fluctuating force exerting on the i -th particle by the surrounding fluid. This fluctuating force must depend on the fluctuating bath molecules as well as the presence of other Brownian particles nearby. Noting Eqs. 4.11 and 4.15, this force must be related with the friction tensors. In order to take the random nature into account as in Eq. 4.11, we define the quantity, \mathbf{f}_i , by the Gaussian fluctuating part:

$$\langle \mathbf{f}_i(t) \rangle = 0 \quad (4.66)$$

and

$$\langle f_{i\alpha}(t_1) f_{j\beta}(t_2) \rangle = \delta_{ij} \delta_{\alpha\beta} \delta(t_2 - t_1) \quad (4.67)$$

where subscripts α and β indicate Cartesian components and δ_{ij} and $\delta_{\alpha\beta}$ are the Kronecker deltas. The magnitude part (\vec{g}_{ij}) of the fluctuating force, which depends on positions of other particles, can be found to be related to the friction tensors (Exercise 4.14):

$$\vec{\gamma}_{ij} = \frac{1}{2k_B T} \sum_k \vec{g}_{ik} \vec{g}_{jk} \quad (4.68)$$

In Eq. 4.65, the suffix, i , can be replaced by a new suffix representing both the particle number and Cartesian coordinates, x, y, z , so that the new suffix runs from 1 to $3N$, forming a $3N$ -dimensional space. Then, the friction tensors is expressed in terms of one $3N \times 3N$ tensor, which is symmetric. If it is constant in time, it can be diagonalized by transforming the coordinates, x_1, x_2, \dots, x_{3N} , and the separation of variables is accomplished.

For a very dilute case, the diffusion coefficient is inversely proportional to the friction constant by Eq. 4.19. Since Eq. 4.65 predicts that the motion of the i -th particle depends on the motion of the j -th particle, the diffusion in a condensed suspension is more complicated. If $F(\mathbf{r}^N, t)$ denotes the distribution function, the diffusion equation is written as, if $\mathbf{F}_i = 0$ for all i ,

$$\frac{\partial F(\mathbf{r}^N, t)}{\partial t} = \sum_{i,j} \nabla_i \cdot \vec{D}_{ij} \cdot \nabla_j F(\mathbf{r}^N, t) \quad (4.69)$$

where \vec{D}_{ij} is the diffusion tensor. The diffusion tensor can be calculated in terms of the velocity correlation function as follows.

$$\vec{D}_{ij} = \frac{1}{2} \int_0^\infty d\tau \lim_{t \rightarrow \infty} \left\langle \frac{d\mathbf{x}_i(t+\tau)}{dt} \frac{d\mathbf{x}_j(t)}{dt} \right\rangle \quad (4.70)$$

Note that the two vectors here form a dyadic product. This relation is suggested by Eq. 4.3, $\langle \{x(t)-x(0)\}^2 \rangle = 2Dt$ in the stationary limit:

$$D = \frac{1}{2} \frac{d}{dt} \int_0^t dt_2 \int_0^t dt_1 \left\langle \frac{dx(t_1)}{dt_1} \frac{dx(t_2)}{dt_2} \right\rangle$$

The integrand of Eq. 4.70 is called the velocity autocorrelation function:

$$\vec{R}_{ij}(\tau) = \lim_{t \rightarrow \infty} \left\langle \frac{d\mathbf{x}_i(t+\tau)}{dt} \frac{d\mathbf{x}_j(t)}{dt} \right\rangle$$

In Eq. 4.65, the tensors, $\vec{\gamma}_{ij}$, depend on positions of Brownian particles and change in time, so that Eq. 4.65 cannot be solved unless a computer is used. However, if those coefficients do not change much within the relaxation time of the Brownian motion, they may be approximated by the initial values. Even under this approximation, the equation of motion is coupled with those for other particles and the separation of variables is required.

In order to illustrate the treatment involved in many Brownian particles, we consider, for simplicity, only two particles, 1 and 2, of the same mass m . Suppose that they are at position \mathbf{x}_1 and \mathbf{x}_2 at t , and subject to fluctuating forces, \mathbf{f}_1 and \mathbf{f}_2 , respectively. These forces include those from liquid as well as forces due to the presence of another particle nearby. By modifying Eq. 4.10, the Langevin equations then read

$$m \frac{d^2 \mathbf{x}_1}{dt^2} = -\vec{\gamma}_{11} \cdot \frac{d\mathbf{x}_1}{dt} - \vec{\gamma}_{12} \cdot \frac{d\mathbf{x}_2}{dt} + \mathbf{f}_1(t) \quad (4.71)$$

$$m \frac{d^2 \mathbf{x}_2}{dt^2} = -\vec{\gamma}_{21} \cdot \frac{d\mathbf{x}_1}{dt} - \vec{\gamma}_{22} \cdot \frac{d\mathbf{x}_2}{dt} + \mathbf{f}_2(t) \quad (4.72)$$

Here, $\vec{\gamma}_{ij}$ ($i, j = 1, 2$) are the friction tensors.

The friction tensors are related to the mobility tensors, \vec{b}_{ij} . The both tensors are symmetric for the equal spherical particles because of symmetry. In order to find the relation between these tensors, consider a general case, when two particles are moving in a viscous fluid with velocities, \mathbf{v}_1 and \mathbf{v}_2 , and hydrodynamic forces, \mathbf{F}_1^H and \mathbf{F}_2^H , acting on them. By definition, we have $\mathbf{F}_i^H = \sum_j \vec{\gamma}_{ij} \cdot \mathbf{v}_j$ and $\mathbf{v}_i = \sum_j \vec{b}_{ij} \cdot \mathbf{F}_j^H$. Therefore, we find (Exercise 4.15)

$$\begin{aligned} \vec{\gamma}_{11} &= \vec{\gamma}_{22} = (\vec{b}_{11} - \vec{b}_{12} \cdot \vec{b}_{22}^{-1} \cdot \vec{b}_{21})^{-1} \\ \vec{\gamma}_{12} &= \vec{\gamma}_{21} = (\vec{b}_{12} - \vec{b}_{11} \cdot \vec{b}_{12}^{-1} \cdot \vec{b}_{22})^{-1} \\ \vec{b}_{11} + \vec{b}_{12} &= (\vec{\gamma}_{11} + \vec{\gamma}_{12})^{-1} \quad \text{and} \quad \vec{b}_{11} - \vec{b}_{12} = (\vec{\gamma}_{11} - \vec{\gamma}_{12})^{-1} \end{aligned} \quad (4.73)$$

Here, the exponent, $^{-1}$, implies the inverse of the dyadic. The mobility tensors depend on the relative position, $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$, as follows (Batchelor, 1976).

$$\vec{\mathbf{b}}_{ij} = \frac{1}{6\pi\eta a} \left[A_{ij} \frac{\mathbf{r}\mathbf{r}}{r^2} + B_{ij} \left(\vec{\mathbf{I}} - \frac{\mathbf{r}\mathbf{r}}{r^2} \right) \right] \quad (4.74)$$

where $r = |\mathbf{r}|$ and $\vec{\mathbf{I}}$ is a unit dyadic. If we choose the z axis along \mathbf{r} all the time, $\mathbf{r}\mathbf{r}/r^2 = \mathbf{k}\mathbf{k}$, $\vec{\mathbf{I}} - \mathbf{r}\mathbf{r}/r^2 = \mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j}$, and the tensor is diagonal. Thus, the coefficient A_{ij} stands for the mobility along \mathbf{r} and B_{ij} is that perpendicular to \mathbf{r} . They are given by, for large separations under stick boundary conditions,

$$\begin{aligned} A_{11} = A_{22} &= 1 - \frac{15}{4\rho^4} + O\left(\frac{1}{\rho^6}\right), & A_{12} = A_{21} &= \frac{3}{2\rho} - \frac{1}{\rho^3} + O\left(\frac{1}{\rho^7}\right) \\ B_{11} = B_{22} &= 1 + O\left(\frac{1}{\rho^6}\right), & B_{12} = B_{21} &= \frac{3}{4\rho} + \frac{1}{2\rho^3} + O\left(\frac{1}{\rho^7}\right) \end{aligned}$$

where $\rho = r/a$. As $\rho \rightarrow 2$ (near contact) these smoothly connect to the following (Russel et al., 1989),

$$\begin{aligned} A_{11} = A_{12} &= 0.775 + 2(\rho - 2) + \dots \\ B_{11} &= 0.891 - \frac{0.388}{\ln(\rho - 2)} + \dots & B_{12} &= 0.490 + \frac{0.144}{\ln(\rho - 2)} \end{aligned}$$

Again, we have that $A_{11} = A_{22}$, etc. Since the mobility tensors are diagonal, the friction tensors are also diagonal.

Now we know that the friction tensors are diagonal in the choice of the z axis in the direction of the interparticle vector, \mathbf{r} , it is convenient to use the coordinate system and denote the Cartesian component by a symbol α , such as the component of \mathbf{x}_1 by $x_{1\alpha}$ or of \mathbf{f}_1 by $f_{1\alpha}$ ($\alpha = x, y, z$), and

$$(\vec{\mathbf{y}}_{11})_{\alpha\alpha} = (\vec{\mathbf{y}}_{22})_{\alpha\alpha} = \gamma_\alpha, \text{ and } (\vec{\mathbf{y}}_{12})_{\alpha\alpha} = (\vec{\mathbf{y}}_{21})_{\alpha\alpha} = \Gamma_\alpha \quad (4.75)$$

Hence, from Eqs. 4.71 and 4.72 we obtain the scalar equations:

$$m \frac{d^2 x_{1\alpha}}{dt^2} = -\gamma_\alpha \frac{dx_{1\alpha}}{dt} - \Gamma_\alpha \frac{dx_{2\alpha}}{dt} + f_{1\alpha} \quad (4.76)$$

$$m \frac{d^2 x_{2\alpha}}{dt^2} = -\gamma_\alpha \frac{dx_{2\alpha}}{dt} - \Gamma_\alpha \frac{dx_{1\alpha}}{dt} + f_{2\alpha} \quad (4.77)$$

These coupled equations can be simplified by the transformation:

$$x_\alpha = x_{1\alpha} + x_{2\alpha}, \text{ and } r_\alpha = x_{2\alpha} - x_{1\alpha} \quad (4.78)$$

Namely, the center of mass, x_α , and the relative position, r_α , move according to

$$m \frac{d^2 x_\alpha}{dt^2} = -(\gamma_\alpha + \Gamma_\alpha) \frac{dx_\alpha}{dt} + f_{1\alpha} + f_{2\alpha} \quad (4.79)$$

$$m \frac{d^2 r_\alpha}{dt^2} = -(\gamma_\alpha - \Gamma_\alpha) \frac{dr_\alpha}{dt} + f_{2\alpha} - f_{1\alpha} \quad (4.80)$$

These equations are of the same form as Eq. 4.10.

Following Eqs. 4.67 and 4.68 (or Eqs. 4.11 and 4.15), we have

$$\langle (f_{1\alpha}(t_1) + f_{2\alpha}(t_1))(f_{1\beta}(t_2) + f_{2\beta}(t_2)) \rangle = 4k_B T (\gamma_\alpha + \Gamma_\alpha) \delta_{\alpha\beta} \delta(t_2 - t_1) \quad (4.81)$$

$$\langle (f_{2\alpha}(t_1) - f_{1\alpha}(t_1))(f_{2\beta}(t_2) - f_{1\beta}(t_2)) \rangle = 4k_B T (\gamma_\alpha - \Gamma_\alpha) \delta_{\alpha\beta} \delta(t_2 - t_1) \quad (4.82)$$

Here we have used that $\frac{1}{2} m \langle x_\alpha^2 \rangle = \frac{1}{2} m \langle v_\alpha^2 \rangle = k_B T$ as $t \rightarrow \infty$. The center of mass moves with velocity $\frac{1}{2} d\mathbf{x}/dt$ ($\mathbf{x} = (x_x, x_y, x_z)$) with mass $2m$. Thus, the $\alpha\beta$ component of the center-of-mass diffusion tensor is given by

$$D_{\alpha\beta}^{(c)} = \frac{2k_B T}{\gamma_\alpha + \Gamma_\alpha} \delta_{\alpha\beta} \quad (4.83)$$

Now, we know that the friction tensor is diagonal in the present coordinate system, so that $\gamma_\alpha + \Gamma_\alpha = (\tilde{\mathbf{y}}_{11} + \tilde{\mathbf{y}}_{12})_{\alpha\alpha} = 1/(\tilde{\mathbf{b}}_{11} + \tilde{\mathbf{b}}_{12})_{\alpha\alpha}$. Hence, we can write Eq. 4.83 as (Exercise 4.16)

$$D_{\alpha\beta}^{(c)} = 2k_B T (\tilde{\mathbf{b}}_{11} + \tilde{\mathbf{b}}_{12})_{\alpha\beta}$$

Or referring to a general choice of the coordinate system,

$$\tilde{\mathbf{D}}^{(c)} = 2k_B T (\tilde{\mathbf{b}}_{11} + \tilde{\mathbf{b}}_{12}) \quad (4.84)$$

where the mobility tensors, $\tilde{\mathbf{b}}$, are given by Eq. 4.73. Similarly, we have the relative (rotational) diffusion tensor:

$$\tilde{\mathbf{D}}^{(r)} = 2k_B T (\tilde{\mathbf{b}}_{11} - \tilde{\mathbf{b}}_{12}) \quad (4.85)$$

The diffusion tensor of individual particles can be easily obtained by noting the transformation of Eq. 4.78, i.e., $\mathbf{x} = \mathbf{x}_1 + \mathbf{x}_2$ and $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$, and Eq. 4.70.

$$\begin{aligned}
\overleftrightarrow{\mathbf{D}}^{(\text{particle1})} &= \frac{1}{2} \int_0^\infty d\tau \lim_{t \rightarrow \infty} \left\langle \frac{d\mathbf{x}_1(t+\tau)}{dt} \frac{d\mathbf{x}_1(t)}{dt} \right\rangle \\
&= \frac{1}{8} \int_0^\infty d\tau \lim_{t \rightarrow \infty} \left[\left\langle \frac{d\mathbf{x}(t+\tau)}{dt} \frac{d\mathbf{x}(t)}{dt} \right\rangle + \left\langle \frac{d\mathbf{r}(t+\tau)}{dt} \frac{d\mathbf{r}(t)}{dt} \right\rangle \right]
\end{aligned}$$

Using Eq. 4.70, again, we can rewrite the two terms by $\overleftrightarrow{\mathbf{D}}^{(c)}$ and $\overleftrightarrow{\mathbf{D}}^{(r)}$. Thus, we have

$$\overleftrightarrow{\mathbf{D}}^{(\text{particle1})} = k_B T \overleftrightarrow{\mathbf{b}}_{11} \quad (4.86)$$

Particle 2 has the similar diffusion tensor. This expression could be important, when many Brownian particles are present, but not so densely.

For two equal spheres in contact (a doublet) we can use the values of A_{ij} and B_{ij} given for Eq. 4.74. Even though they are singular in the limit of $\rho \rightarrow 2$, we have

$$\overleftrightarrow{\mathbf{D}}^{(c)} = \frac{k_B T}{3\pi\eta a} \left[1.38 \overleftrightarrow{\mathbf{I}} + 0.17 \frac{\mathbf{r}\mathbf{r}}{r^2} \right], \quad \overleftrightarrow{\mathbf{D}}^{(r)} = \frac{0.401 k_B T}{3\pi\eta a} \left(\overleftrightarrow{\mathbf{I}} - \frac{\mathbf{r}\mathbf{r}}{r^2} \right) \quad (4.87)$$

These results well predicted experimental values of Vadas et al. (1976) for a short time interval of about 0.1 sec with polystyrene latex of diameter of about 1 or 2 μm .

4.2 Response to a Static Electric Field

If an electric field, \mathbf{E} , is applied to an atom at rest, the electric force displaces atomic nucleus and electrons into mutually opposite directions. The atom is usually not ionized, but the displacement causes the separation of the positive and negative charges within the atom and induces an electric dipole moment. If the atom is neutral, the positive and the negative displaced charges in the atom are of the same absolute magnitude, q . If the average distance between them is denoted by \mathbf{x} , oriented in the direction of \mathbf{E} , the induced dipole moment, \mathbf{p} , is defined by $q\mathbf{x}$. This induced dipole locally produces an electric field around and, accordingly, modifies the applied field. The strength of the induced dipole is proportional to that of the applied field, unless it is very large, so that $\mathbf{p} = \alpha\mathbf{E}$. The proportionality constant, α , is called as the atomic polarizability.

There are many atoms in a particle. For simplicity, we assume that the internal structure of the particle is uniform. Each atom in the particle is polarized under an external electric field. Each of the induced dipoles introduces an additional field at the other atoms. Therefore, the external field is modified inside and out-

side the particle. The net modification is equivalent to the following. In the particle, the displaced charges of one atom cancel with the opposite charges displaced in the nearest neighboring atom, so that no charge separation occurs as a whole, in the macroscopic scale, inside the particle except on the surface of the particle. The charges appearing without cancellation on the surface are called as the polarization charges and are after all responsible for the modification of the applied field inside and in the outside neighborhood of the particle. The magnitude, the sign, and the distribution of the polarization charges on the surface depend on the material, the size, the shape, and the relative orientation of the particle.

We can describe the behavior of the induced atomic dipoles in a different way. First, we make the particle size infinitely large, so that the presence of the surface need not to be considered. In addition, we assume that the atoms are distributed uniformly far apart from each other. The modification of the external field due to the neighboring induced dipoles is thus uniform and small. We can add the dipole moments \mathbf{p} per unit volume and call the sum the polarization vector \mathbf{P} . Since $\mathbf{p} = \alpha\mathbf{E}$ (\mathbf{E} : the modified net field), in the MKS system of units, we have

$$\mathbf{P} = N\alpha\mathbf{E} \quad (4.88)$$

where N is the number density of atoms. The quantity, $N\alpha$, is called the electric susceptibility, χ_e . Equivalently, we can introduce the dielectric constant, ϵ , defined by

$$N\alpha = \chi_e = (\epsilon - 1)\epsilon_0 \quad (4.89)$$

where ϵ_0 is the permittivity of free space. The reason of this introduction is that \mathbf{E} is the sum of the external field (or the field due to external charges) and the field due to polarization charges. But the polarization charges are unknown unless the total electrostatic problem has been solved. Usually, the distribution of the external charges, or, more exactly speaking, the so-called free charges, such as freely movable electrons and ions, is known. If we define another field vector, \mathbf{D} (the electric displacement vector), by $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P} = \epsilon\epsilon_0\mathbf{E}$, $\nabla \cdot \mathbf{D}$ is directly related to the free charges. Therefore, the \mathbf{D} vector is an important field quantity when a polarizable material is present.

Now, for a spherical particle under a uniform electric field, \mathbf{E}_0 (at an infinite distance), the polarization inside is uniform and \mathbf{P} everywhere. \mathbf{P} is in the direction of \mathbf{E}_0 . The surface polarization charge density is given by P_n , the outward normal component of \mathbf{P} . This surface charge produces an electric field, $-\mathbf{P}/3\epsilon_0$, inside the medium and modifies \mathbf{E}_0 . Thus, the field which induces atomic dipoles inside the sphere is $\mathbf{E} = \mathbf{E}_0 - \mathbf{P}/3\epsilon_0$. On the other hand, if the dielectric constant of the particle is ϵ , Eqs. 4.88 and 4.89 lead to $\mathbf{P} = (\epsilon - 1)\epsilon_0\mathbf{E}$, so that we have $\mathbf{P} = (\epsilon - 1)\epsilon_0(\mathbf{E}_0 - \mathbf{P}/3\epsilon_0)$. By solving for \mathbf{P} we find

$$\mathbf{P} = \frac{3(\epsilon - 1)}{\epsilon + 2}\epsilon_0\mathbf{E}_0 \quad (4.90)$$

The electric field outside the sphere is the applied field, \mathbf{E}_o , plus the field due to the electric dipole moment:

$$\mathbf{p} = 4\pi \frac{\varepsilon - 1}{\varepsilon + 2} a^3 \varepsilon_o \mathbf{E}_o \quad (4.91)$$

where a is the radius. The dipole moment is located at the center of the sphere. The magnitude is proportional to the volume.

We note that the polarity of the surface charge depends on the surrounding. If the dielectric constant is larger in the surrounding medium, it will be reversed.

4.3 Response to a Time-dependent Electric Field

Light scattering experiments can provide much information on Brownian particles (see Chapt. 6). Light is an electromagnetic wave, $\mathbf{E}(\mathbf{x}, t) = \mathbf{E}_o e^{i(n\mathbf{k} \cdot \mathbf{x} - \omega t)}$ at position \mathbf{x} and time t , where i is the imaginary number, n is the index of refraction of the medium, \mathbf{k} is the wave vector in vacuum ($|\mathbf{k}| = 2\pi/\lambda$, λ : wavelength), ω is the angular frequency ($2\pi\nu$, ν : frequency). The polarization in the medium occurs due to the induced displacement of charges. Since the charge carriers (mostly electron, but sometimes ions) have finite masses, the response to the field has always a time lag, which depends on frequency. Thus, the relation between \mathbf{D} and \mathbf{E} vectors, $\mathbf{D} = \varepsilon_o \varepsilon \mathbf{E}$, must be explicitly rewritten as

$$\mathbf{D}(\mathbf{x}, \omega) = \varepsilon_o \varepsilon(\omega) \mathbf{E}(\mathbf{x}, \omega) \quad (4.92)$$

where $\mathbf{D}(\mathbf{x}, \omega)$ and $\mathbf{E}(\mathbf{x}, \omega)$ are respectively the Fourier transforms of $\mathbf{D}(\mathbf{x}, t)$ and $\mathbf{E}(\mathbf{x}, t)$ with respect to time.

The frequency dependence of ε can be classically understood as follows. For simplicity, consider that the frequency of the incident light is in the optical region, so that only optical (outer most) electrons of atoms are displaced away from the remaining ions (atomic core). Suppose that an electron of charge e and mass m is harmonically bound to the ion. In the optical region, the wavelength of the plane wave is much larger than the atomic size. Therefore, the field is always uniform over the atom and the field acting on the electron can be represented by the field at the center of the atom. We write the field at the atom as $\mathbf{E}_a e^{-i\omega t}$. Then, the equation of motion of the electron under the electric field is given by

$$m \frac{d^2 \mathbf{x}}{dt^2} = -m\gamma_o \frac{d\mathbf{x}}{dt} - m\omega_o^2 \mathbf{x} + e\mathbf{E}_a e^{-i\omega t} \quad (4.93)$$

where \mathbf{x} , $m\gamma_o$, and $m\omega_o^2 \mathbf{x}$ are the displacement, the damping coefficient, and the restoring force of the electron, respectively. This equation is a forced oscillation

and the damping term is due to the fact that an accelerating charge always loses its kinetic energy due to radiation (Jackson, 1975). The solution of Eq. 4.93 is, after the transient term dies down because of the damping, given by

$$\mathbf{x}(t) = \frac{e\mathbf{E}}{m} \frac{1}{\sqrt{(\omega_o^2 - \omega^2)^2 + (\gamma_o\omega)^2}} e^{-i(\omega t - \phi)} \quad (4.94)$$

with

$$\phi = \tan^{-1} \frac{\gamma_o\omega}{\omega_o^2 - \omega^2}$$

The quantity, ϕ , is the phase shift due to the damping. Now, we note that the amplitude of $\mathbf{x}(t)$ is largest when $\omega = \omega_o$. Hence, we call ω_o the resonant frequency. For an atomic case, ω_o is at least about 10^{15} sec^{-1} . For ions bound in a molecules or in a solid, ω_o is a vibrational frequency of about 10^{13} sec^{-1} . For rotating molecular dipoles, the value of γ_o is of the order of 10^8 sec^{-1} . Eq. 4.94 shows that if the frequency ω is far from ω_o the interaction between the incident plane wave and the charge is small.

There are many (discrete, i.e. well separated) frequencies, ω_k ($k = 1, 2, \dots$), at which light absorption occurs, in an atom. The frequency corresponds to a radiative transition, in the present case of the optical electrons, from the lowest energy level to one of many excited states. Each of these frequencies individually contributes to the displacement of the optical electrons. Therefore, the total displacement is given by the sum of the coefficients of Eq. 4.94, replaced ω_o by ω_k . In order to explicitly express the frequency-dependence, we take the Fourier transform on both sides of the resulting equation. By noting that the induced dipole moment is expressed as $\mathbf{p}(\omega) = e\mathbf{x}(\omega)$ and Eq. 4.94, the frequency-dependent dielectric constant can be written as

$$\varepsilon(\omega) = 1 + \varepsilon_m(\omega) + \frac{e^2 N}{m\varepsilon_o} \sum_{k=0}^{\infty} \frac{f_k}{\omega_k^2 - \omega^2 - i\gamma_k\omega} \quad (4.95)$$

where ε_m is the contribution of rotational and vibrational modes of molecular permanent dipole moments. The contribution is usually very small in the optical region. If the particle is metallic and contains free electrons, these free electrons will also contribute to $\varepsilon(\omega)$ with vanishing characteristic frequency. In Eq. 4.95, N is the number of atoms per unit volume and f_k is a fraction expressing the magnitude of the contribution from ω_k . This quantity, f_k , is called the oscillator strength and satisfies the sum rule:

$$\sum_{k=0} f_k = Z_o \quad (4.96)$$

where Z_0 is the number of optical electrons in the atom. The summation must also cover the optical transition to continuum spectra. The values of f_k , ω_k , and γ_k may be quantum-mechanically calculated or experimentally obtained (see Sec. 8.2). In Sec. 1.2, the size-dependent behavior of metallic particles is discussed. Their free electrons exhibit characteristic plasma oscillations, leading to optical selective absorption of particular frequencies (Kleeman, 1968).

4.4 Response to Mechanical Stress

The importance of mechanical behavior of a colloidal dispersion becomes clear in the applications. For instance, the “apparent viscosity” of a paint must change quickly during its brushing, if it is a good paint. Namely, the paint must be held well in the brush (high viscosity), but flow freely (low viscosity) on a surface when being painted, so that no brush mark is left. A high speed printing (news-paper, chips printing circuit, etc.) requires a similar characteristic in the ink to be used. The required behavior is strongly related with the time-dependent nonlinear relation between the shear stress and strain of the disperse system. The rheological approach may be used, although has not been so well advanced, in this field of study. Therefore, we limit ourselves to the linear theory (Ferry, 1980). In fact, the viscosity can depend on shear strain, but much of the early work on viscoelasticity was based on the notion that a material generally responds as a combination of a Newtonian fluid (linearity between stress and rate of strain) and a Hookean solid (linearity between stress and strain).

In a Newtonian fluid, consider a fluid flow in the direction of x with its gradient along y . Then, the viscosity, η , is defined by

$$F_{xy} = \eta(dv_x/dy) \quad (4.97)$$

where F_{xy} is the shear stress, the force, in the direction of v_x , acting tangentially per unit area, whose normal direction is along y . If the shear strain, $e_{xy} = d\Delta x/dy$, is the rate of change along y of the displacement, Δx , dv_x/dy is the temporal rate of the shear strain, de_{xy}/dt , since $v_x = d\Delta x/dt$. Note that if v_x is a uniform flow along the x direction of the fluid, then the displacement Δx due to the flow is uniform along the flow. If the flow is constant in time, Δx uniformly increases in time.

However, the disperse system does not behave like a Newtonian fluid, since it exhibits an effect of memory. Suppose that a strain is defined by

$$e_{xy}(t) = 1 \text{ for } t > t_0 \text{ and } 0 \text{ for } t < t_0$$

Then, it can be expressed by a unit step function as

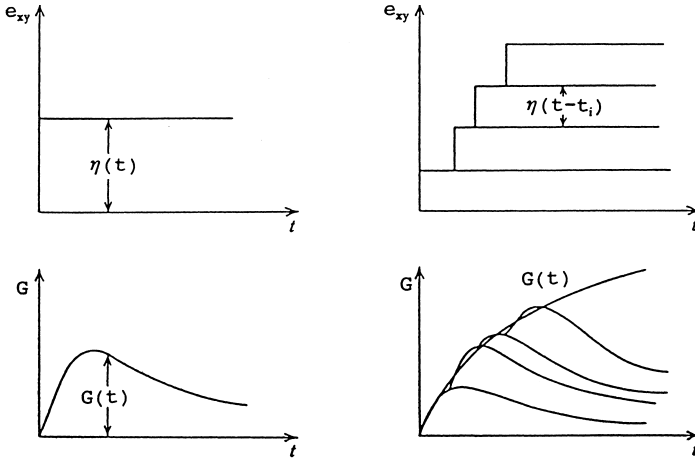


Fig. 4.2 Relaxation modulus, $G(t-t')$.

$$e_{xy}(t) = \eta(t - t_0) \quad (4.98)$$

This is an abrupt change of the strain at $t = t_0$. We have that $de_{xy}/dt = \delta(t-t_0)$, the Dirac δ function. The δ function is defined by

$$\delta(t - t_0) = 0 \text{ for } t \neq t_0 \quad (4.99)$$

$$\int_{-\infty}^{\infty} \delta(t - t') dt' = 1 \quad (4.100)$$

The responding stress to this impulse starts at t_0 , as shown in Fig. 4.2 ($t_0 = 0$), and continues as expressed by $G(t-t_0)$, a characteristic memory function of the disperse system called the (shear) relaxation modulus. This vanishes for $t < t_0$ because of causality.

If the strain $e_{xy}(t)$ is a continuous function of time and if the linear theory can be assumed to hold, the response at t can be expressed by the linear sum of the effects of the strains acting on the system before t , as follows.

$$F_{xy}(t) = \int_{-\infty}^t G(t - t') \frac{d}{dt'} e_{xy}(t') dt' \quad (4.101)$$

In general, the work done by the stress is partly stored in the system and partly lost as heat. Consider that the strain, denoted by e , behaves as

$$e(t) = e_0 \sin \omega t \quad (4.102)$$

where e_0 is a constant. According to Eq. 4.101 the response, $\sigma(t)$, can be written as

$$\sigma(t) = e_0(G' \sin \omega t + G'' \cos \omega t) \quad (4.103)$$

where

$$G' = \omega \int_0^\infty G(\tau) \sin \omega \tau d\tau \text{ and } G'' = \omega \int_0^\infty G(\tau) \cos \omega \tau d\tau \quad (4.104)$$

The integrals converge since $G(\tau)$ vanishes as $\tau \rightarrow \infty$, if the system is a fluid. This is because any fluid cannot permanently support a stress. In Eq. 4.103, G' is in phase with the strain $e(t)$, while G'' is out of phase by $\pi/2$ or in phase with de/dt and related to the viscous term. Therefore, G' is called the dynamic or storage modulus, while G'' is the dynamic loss or the loss modulus. The ratio G''/G' is called the loss tangent:

$$\text{The loss tangent} = G''/G' \equiv \tan \delta \quad (4.105)$$

There are mechanical models for the strain-stress relation called the Maxwell and the Voigt model. The former model consists of a mechanical spring and a dashpot in series, while the latter model has both of them in parallel rather than in series (Figs. 4.3 and 4.4). In the Maxwell model the strain indefinitely increases in time under a constant external force (stress), so that it is an appropriate model for elastic sols. On the other hand, in the Voigt model the strain is kept finite under a constant external force (stress) and comes to an equilibrium, so that this model is suitable for handling the elasticity of a solid-like system.

In the Maxwell model, an abrupt strain (deformation) in the model can occur since the spring can immediately respond to an external force (stress) without an immediate response at the dashpot (the viscous force at the dashpot is very large if it tries to abruptly move). Suppose that the total strain applied is a step function (Eq. 4.98). After the application the stress must be the same at both the spring and the dashpot all the time, so that the strain at the dashpot gradually increase and that at the spring gradually decrease (the total strain is constant). Therefore, the stress decreases in time and finally vanishes. This behavior is exactly the same as the temporal decrease in the charging current of a series RC circuit when

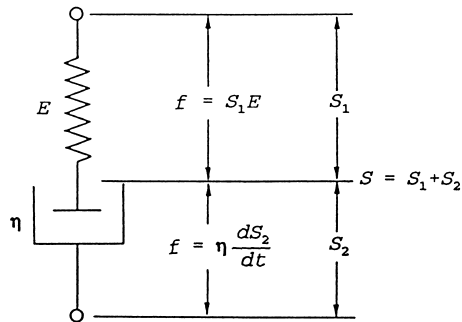


Fig. 4.3 The Maxwell model.
 E : Elastic modulus, η : Viscosity, f : Force,
 S_1, S_2 : Strain.

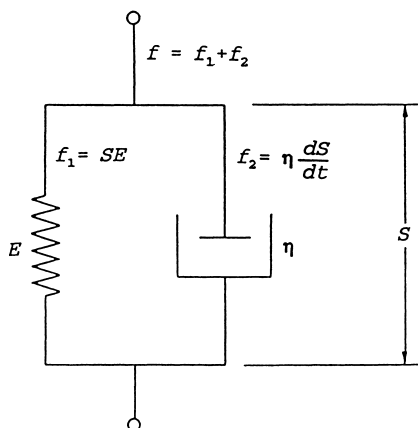


Fig. 4.4 The Voigt model

E : Elastic modulus, η : Viscosity, f_1, f_2 : Force, S : Strain.

it is connected to a constant battery. The energy loss here occurs in the resistor, while it does in the dashpot in the Maxwell model.

In the Voigt model, an abrupt strain (deformation) cannot occur. (Exercise 4.22). It increases from zero to a final constant value when a constant total force is applied at time t_0 to the model.

However, it is usually necessary to model an elastic behavior of a disperse system by combining both the Maxwell and Voigt type in various ways, so that the resulting model can correctly describe the behavior. For instance, a model of a dashpot in series with a Voigt type may represent a viscoelastic fluid and a model of a spring connected in series to a Maxwell type can describe some viscoelastic solid.

Mellema et al. (1987) measured the linear viscoelastic response of dispersions of silica spheres of two radii, 28 ± 2 nm and 76 ± 2 nm, at a volume fraction of 0.45 and obtained results in a good correlation with the viscoelastic fluid model.

The rheological studies of dispersions are a rapidly expanding field and recent instrumentation includes the *shear rheometer*. Suppose that a disperse fluid is located between two parallel plates and one of the plates is subject to a parallel rapid, short-lived displacement. The resultant stress on the other plate will not be experienced immediately, but only after a certain delay time (Δt). By measuring the delay time as a function of the separation of the plates, the velocity of propagation of the shear wave can be determined. This is the principle of the shear rheometer. If the short-lived displacement is replaced by a sinusoidal oscillation, the response of the other plate may be recorded. The two parallel plates can be converted to two concentric cylinder. The variation of the time lag in the response with frequency provides information on the processes responsible for the dissipation of energy which occurs as the individual elements of material respond to the continuously varying stress. The principles involved in this technique are essentially similar to those governing the response of dielectric materials to a fluctuating electric field, and the results are analyzed in an analogous fashion to identify the rheological storage and loss factors. These in turn can be related to the nature of the interparticle forces in a disperse system.

Exercises

- 4.1** The size of a nonspherical particle is sometimes represented by the radius of gyration, r_G . It is defined by

$$r_G^2 = \frac{\int r^2 \rho dV}{\int \rho dV}$$

where ρ is the density and r is the distance from the center of gravity of the particle (Tanford, 1961). Calculate of the radius of gyration of a sphere and an oblate and a prolate ellipsoid of revolution (see Table 4.1).

- 4.2** Does or does not the perpetual Brownian motion violate the second law of thermodynamics?
- 4.3** Suppose that small particles are dispersed in a liquid in thermal equilibrium under gravity. The number density N of the particles at a height h above h_0 is given by

$$N = N_0 \exp[(m - m')g(h - h_0)/k_B T]$$

where N_0 is the number density at height h_0 and m' is the mass of the fluid displaced by the particle of mass m . Note that J. Perrin used the above relation to determine the value of k_B with a monodisperse system. (Another method for determining k_B is to use Eq. 4.18).

- 4.4** Consider a spherical solid particle of radius, a , and density, ρ_s , in a liquid of density, ρ_l . Find and solve the equation of motion of the particle before it settles in gravity.
- 4.5** Dynamic collisions can be defined as when linear or angular momentum transfer occurs just like in the Langevin equation. Under what conditions can collisions be independent from other collisions? Consider in terms of the relaxation constant appearing in the Langevin equation.
- 4.6** Derive Eq. 4.6. Now, consider that $\langle \mathbf{r}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$, where $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$. Suppose that the particle moves in the x direction during $t/3$, then in the y direction during the following $t/3$, and then in z during the remaining $t/3$ of the total time t . Then, $\langle \mathbf{r}^2 \rangle = 2Dt$ by using Eq. 4.3, instead of Eq. 4.6. Is there something wrong in the reasoning?
- 4.7** Happel and Brenner give for an ellipsoid of revolution with major semiaxis, a , and minor semiaxis, b , when moving along the symmetry axis,

$$D_{\parallel} = \frac{k_B T}{8\pi\eta a} \frac{1}{1 - \rho^2} \left(\frac{2 - \rho^2}{\sqrt{1 - \rho^2}} \ln \frac{1 + \sqrt{1 - \rho^2}}{\rho} - 1 \right), \left(\rho = \frac{b}{a} < 1 \right)$$

$$= \frac{k_B T}{8\pi\eta a} \frac{\rho}{1 - \rho^2} \left(\frac{2 - \rho^2}{\sqrt{\rho^2 - 1}} \tan^{-1} \sqrt{\rho^2 - 1} - 1 \right), \left(\rho = \frac{a}{b} > 1 \right)$$

These are exact. Show that these relations approach to the Stokes law for a sphere ($\rho = 1$). Comparing with the corresponding results for the angle-averaged diffusion coefficients, find the corresponding expressions for D_{\perp} , when moving perpendicular to the symmetry axis. (Note Eq. 4.22 and Table 4.1).

- 4.8** Verify Eq. 4.44.
- 4.9** Show that the distribution function, Eq. 4.41, is normalized for any $t > 0$.
- 4.10** Referring to Eq. 4.47 for an ellipsoid of revolution, if ρ is very small, it should stand for a long rod. If ρ is very large compared with unity, it will be for a very thin disc. Find the rotational diffusion coefficients for the limiting cases.
- 4.11** Verify Eq. 4.50. How should this be modified under slip boundary conditions?
- 4.12** If a translational motion of a particle in a liquid is accompanied by a drag given by Eq. 4.53, find the diffusion coefficient by Eq. 4.22a.
- 4.13** Show that Eq. 4.64 is normalized at $t=0$.
- 4.14** Establish Eq. 4.68 by using the definition of Eq. 4.67.
- 4.15** Establish equations in Eq. 4.73.
- 4.16** Obtain Eq. 4.83.
- 4.17** In finding the result of Eq. 4.86, show that the cross correlation between the velocity of the center of mass, $d\mathbf{x}(t)/dt$, and the rotational velocity, $d\mathbf{r}(t)/dt$, vanishes.
- 4.18** Using Eq. 4.86 and assuming the pairwise additivity of the hydrodynamic interaction among Brownian particles, find the diffusion tensor.
- 4.19** Using Eq. 4.94, calculate the work done by the field on the oscillator. This work is related to light absorption and emission. Distinguish the cases of absorption and emission.
- 4.20** In Eq. 4.101, show that, if $e_{xy}(t) = \eta(t-t_0)$, the response is given by $G(t-t_0)$.
- 4.21** Show that G'' of Eq. 4.104 corresponds to a viscosity representing the energy loss.
- 4.22** Show that an abrupt strain (displacement) cannot occur in the Voigt model.

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